Ninth Edition

Student Solutions Manual to Accompany The Systematic Identification of Organic Compounds

Christine K. F. Hermann • Terence C. Morrill
Ralph L. Shriner • Reynold C. Fuson

WILEY

STUDENT SOLUTIONS MANUAL TO ACCOMPANY THE SYSTEMATIC IDENTIFICATION OF ORGANIC COMPOUNDS

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Preface

For the first six editions of this textbook, no solutions manual was available. As some of the problems presented throughout the textbook are quite difficult, I wrote the solutions manual as an aid to users of the textbook. The textbook contains no problems in Chapters 1, 2, 3, and 12.

I would like to thank Terence Morrill for the answers to Problem Sets 6–20 in Chapter 13, which is available on a companion website. These answers had been in handwritten form for many years. I would like to thank Danielle Davis for her assistance in writing the solutions manual for the seventh edition. I would like to thank Stephen Pond for his patience and support during the preparation of this edition.

Christine K. F. Hermann
Radford University

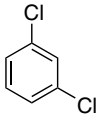
Chapter 4

Preliminary Examination, Physical Properties, and Elemental Analysis

1. Use the values for a nonassociated liquid.

$$\text{corr bp} = 167 + \frac{760-650\text{mm}}{10\text{mm}}\left\{\left(\frac{0.56-0.50}{200-150}\times(167-150)\right)+0.50\right\}$$

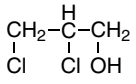
$$= 172.72$$

1,3-dichlorobenzene 

2. Use the values for an associated liquid.

$$\text{corr bp} = 180 + \frac{760-725\text{mm}}{10\text{mm}}\left\{\left(\frac{0.46-0.42}{200-150}\times(180-150)\right)+0.42\right\}$$

$$= 181.55$$

2,3-dichloro-1-propanol 

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3. 285 °C

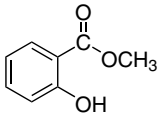
4. 410 °C

5. Methyl acetate > methyl thioacetate

6. 2-Methyl-2-pentanol < 3-methyl-2-pentanol < 2-hexanol < 1-hexanol

7. $\text{sp gr}\,\frac{20}{4} = \frac{0.989}{0.834} = 1.186$

$\text{sp gr}\,\frac{20}{4} = \frac{0.989}{0.834} \times 0.99823 = 1.184$

methyl salicylate 

8. Bromomethane < bromoethane < 1-bromopropane < 1-bromobutane < 1-bromopentane < 1-bromohexane

9. 4-Octene > 3-octene > 2-octene > 1-octene

10. Ethyl propyl ether < 1-pentanamine < 1-pentanol < pentanal < methyl butanoate < pentanoic acid

11. $n_D^{20} = 1.430 + \left[(35-20)(0.00045)\right] = 1.437$

12. $\left[\alpha\right]_D^{25^\circ} = \frac{26.6}{(2.5\text{cm})\left(\frac{10\text{cm}}{1\text{dm}}\right)\left(\frac{0.8\text{g}}{50\text{mL}}\right)} = 66.5, \text{ sucrose}$

13. $\text{Optical purity} = \frac{6.00-4.00}{6.00+4.00} \times 100 = 20.00\%$

$\text{Observed rotation} = +30.00 \times 0.200 = +6.00^\circ$

$\%\,\text{ee} = \frac{+6.00}{+30.00} \times 100 = 20.00\%$

$\%\,\text{of}\,(+)\text{isomer} = \frac{4.00}{6.00+4.00} \times 100 = 40.00\%$

$\%\,\text{of}\,(-)\text{isomer} = \frac{6.00}{6.00+4.00} \times 100 = 60.00\%$

14. Methylene chloride with ether, toluene, or hydrocarbons as co-solvents

15. Methanol; ethanol

16. $\text{mg of C} = 10.71\text{ mg of } CO_2 \times \frac{12.011\text{ C}}{44.009\ CO_2} = 2.92\text{ mg of C in sample}$

$$\%C = \frac{2.92\text{ mg of C}}{13.66\text{ mg of sample}} \times 100 = 21.38\%\text{ of C}$$

$$\text{mg of H} = 3.28\text{ mg of } H_2O \times \frac{2.016\text{ H}}{18.015\ H_2O} = 0.367\text{ mg of H in sample}$$

$$\%H = \frac{0.367\text{ mg of H}}{13.66\text{ mg of sample}} \times 100 = 2.69\%\text{ of H}$$

$$\%Br = \frac{3.46\text{ mg of H}}{4.86\text{ mg of sample}} \times 100 = 71.19\%\text{ of Br}$$

$$\%O = 100 - (21.40 + 2.69 + 71.19) = 4.72\%\text{ of O}$$

$$C = \frac{21.40}{12.011} = 1.782 \qquad \frac{1.782}{0.295} = 6.04$$

$$H = \frac{2.669}{1.0080} = 2.669 \qquad \frac{2.669}{0.295} = 9.05$$

$$Br = \frac{71.19}{79.904} = 0.891 \qquad \frac{0.891}{0.295} = 3.02$$

$$O = \frac{4.72}{15.999} = 0.295 \qquad \frac{0.295}{0.295} = 1.00$$

Empirical formula = $C_6H_9Br_3O$
Empirical weight = 336.86
Molecular formula = $C_{12}H_{18}Br_6O_2$

17. **a.** $C_6H_{12}O_2$
$U = 6 + 1 - ½\ (12) + ½\ (0) = 1$
One double bond; *or* one ring

b. $C_5H_{10}Cl_2$
$U = 5 + 1 - ½\ (12) + ½\ (0) = 0$
No double bonds, triple bonds, *or* rings

c. $C_7H_{13}N$
$U = 7 + 1 - ½\ (13) + ½\ (1) = 2$
Two rings; *or* two double bonds; *or* one ring and one double bond; *or* one triple bond

d. $C_{12}H_{10}$
$U = 12 + 1 - ½\ (10) + ½\ (0) = 8$
Benzene plus three rings; *or* benzene plus three double bonds; *or* benzene plus two rings and one double bond; *or* benzene plus two double bonds and one ring; *or* benzene plus one triple bond and one double bond; *or* benzene plus one triple bond and one ring

Chapter 5

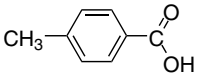
Classification of Organic Compounds by Solubility

1. a. N – alcohols, aldehydes, ketones, esters with one functional group and more than five but fewer than nine carbons, ethers, epoxides, alkenes, alkynes, some aromatic compounds (especially those with activating groups).

b. S_1 – monofunctional alcohols, aldehydes, ketones, esters, nitriles, and amides with five carbons or fewer.

c. A_2 – weak organic acids; phenols, enols, oximes, imides, sulfonamides, thiophenols, all with more than five carbons; β-diketones; nitro compounds with α-hydrogens.

2. a. Insoluble in water, soluble in 5% sodium hydroxide solution, soluble in 5% sodium bicarbonate solution.

4-methylbenzoic acid 

b. Soluble in water and ether, litmus paper turned blue.

butylamine $CH_3CH_2CH_2CH_2NH_2$

c. Insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid solution.

3-heptene $CH_3CH_2CH{=}CHCH_2CH_2CH_3$

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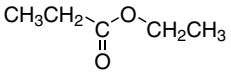
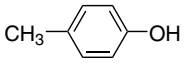
d. Soluble in water and ether; litmus paper is unchanged in color.

ethyl propanoate 

e. Soluble in water and ether; litmus paper is unchanged in color.

propanenitrile $CH_3CH_2C{\equiv}N$

f. Insoluble in water and 5% sodium bicarbonate solution, but soluble in 5% sodium hydroxide solution.

4-methylphenol 

3. a. A_1

b. S_B

c. N

d. S_1

e. S_1

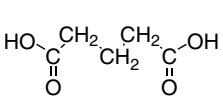
f. A_2

4. Both acyl halides and anhydrides react with water, so any results would be of the carboxylic acid that is formed from the hydrolysis of these compounds.

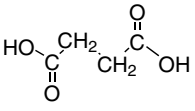
5. a. 1-Propanol is more soluble in water than diethyl ether. 1-Propanol can hydrogen bond with water, whereas diethyl ether does not hydrogen bond with water.

$CH_3CH_2CH_2OH$	$CH_3CH_2OCH_2CH_3$
1-propanol	diethyl ether

b. Pentanedioic acid is more soluble in water than butanedioic acid. Odd carbon number of dioic acids have less intracrystalline forces than even carbon number of dioic acids.

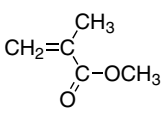


pentanedioic acid

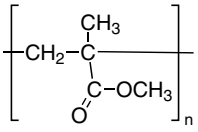


butanedioic acid

c. Methyl methacrylate is more soluble in water than poly(methyl methacrylate). Polymers are insoluble in water.

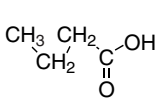


methyl methacrylate

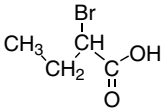


poly(methyl methacrylate)

d. Butanoic acid is more soluble in water than 2-Bromobutanoic acid. The addition of halogens increases the molecular weight and decreases the solubility.

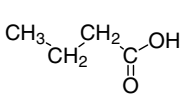


butanoic acid

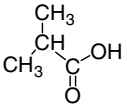


2-bromobutanoic acid

e. 2-Methylpropanoic acid is more soluble in water than butanoic acid. Branching lowers the boiling point and lowers intermolecular forces. Thus, a branched compound is more soluble in water than a straight chain molecule.



butanoic acid

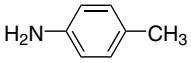


2-methylpropanoic acid

6. a. 1-Chlorobutane is insoluble in water since it is an haloalkane. It is insoluble in 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 96% sulfuric acid solution. Thus 1-chlorobutane is in solubility class I.

1-chlorobutane $CH_3CH_2CH_2CH_2Cl$

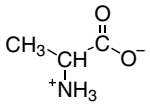
b. 4-Methylaniline is insoluble in water since it is an aniline. It is basic, due to the presence of the amino group, and therefore is insoluble in 5% sodium hydroxide solution, but soluble in 5% hydrochloric acid solution, and thus 4-methylaniline is in solubility class B.

4-methylaniline 

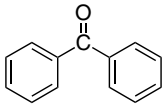
c. 1-Nitroethane is insoluble in water since it is a weak organic acid. It is soluble in 5% sodium hydroxide solution, but insoluble in 5% sodium bicarbonate solution, and thus 1-nitroethane is in solubility class A_2.

1-nitroethane $CH_3CH_2NO_2$

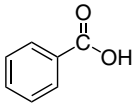
d. Alanine is an amino acid, thus is amphoteric, and soluble in water. Alanine is insoluble in ether and thus in solubility class S_2.

alanine 

e. Benzophenone is insoluble in water because it has more than five carbon atoms. Since it is a neutral compound, containing only carbon, hydrogen, and oxygen, it is insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution. It is soluble in 96% sulfuric acid solution. Therefore, benzophenone is in solubility class N.

benzophenone 

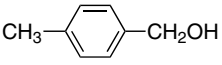
f. As a strong organic acid, benzoic acid is insoluble in water, soluble in 5% sodium hydroxide solution, and soluble in 5% sodium bicarbonate solution. Therefore, benzoic acid is in solubility class A_1.

benzoic acid 

g. As a saturated hydrocarbon, hexane is insoluble in water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 95% sulfuric acid. Hexane is in solubility class I.

hexane $CH_3CH_2CH_2CH_2CH_2CH_3$

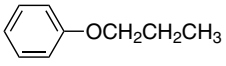
h. 4-Methylbenzyl alcohol is insoluble in water since it has more than five carbon atoms. It is a neutral compound with only carbon, hydrogen, and oxygen. It is insoluble in water, 5% sodium hydroxide solution and 5% hydrochloric acid solution. However, 4-methylbenzyl alcohol is soluble in 96% sulfuric acid and thus in solubility class N.

4-methylbenzyl alcohol 

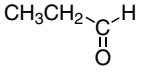
i. As an amine with less than six carbons, ethylmethylamine is soluble in water. It is soluble in ether and its aqueous solutions turn litmus paper blue, therefore it is basic. Ethylmethylamine is in solubility class S_B.

ethylmethylamine $CH_3NHCH_2CH_3$

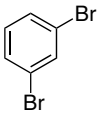
j. Propoxybenzene is insoluble in water because it has more than five carbon atoms. It is a neutral compound with only carbon, hydrogen, and oxygen and is insoluble in 5% sodium hydroxide solution, and 5% hydrochloric acid solution. However, propoxybenzene is soluble in 96% sulfuric acid solution and in solubility class N.

propoxybenzene 

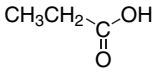
k. Propanal is soluble in water because it has less than five carbons. As a neutral compound, it is soluble in ether and its aqueous solutions do not change the color of litmus paper. Propanal is in solubility class S_1.

propanal 

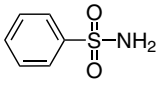
l. As an aryl halide, 1,3-Dibromobenzene is insoluble in water, 5% sodium hydroxide solution, 5% hydrochloric acid solution, and 96% sulfuric acid. 1,3-Dibromobenzene is in solubility class I.

1,3-dibromobenzene 

m. Propanoic acid is soluble in water because it contains less than five carbon atoms. It is soluble in ether, but its aqueous solutions turn litmus paper red. Propanoic acid is in solubility class S_A.

propanoic acid 

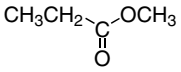
n. As a weak organic acid, benzenesulfonamide is insoluble in water. It is soluble in 5% sodium hydroxide solution but insoluble in 5% sodium bicarbonate solution. Benzenesulfonamide is in solubility class A_2.

benzenesulfonamide 

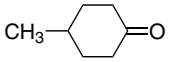
o. 1-Butanol is soluble in water because it contains less than five carbon atoms. It is soluble in ether and its aqueous solutions do not change the color of litmus. 1-Butanol is in solubility class S_1.

1-butanol $CH_3CH_2CH_2CH_2OH$

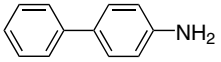
p. Methyl propanoate is soluble in water since it contains less than five carbon atoms. It is soluble in ether and its aqueous solutions do not change the color of litmus. Methyl propanoate is in solubility class S_1.

methyl propanoate 

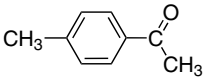
q. 4-Methylcyclohexanone is insoluble in water since it contains more than five carbon atoms. It is also insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid. Therefore, 4-methylcyclohexanone is in solubility class N.

4-methylcyclohexanone 

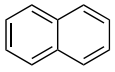
r. Since 4-Aminobiphenyl is an aniline, it is insoluble in water. It is insoluble in 5% sodium hydroxide solution, but soluble in 5% hydrochloric acid solution. 4-Aminobiphenyl is in solubility class B.

4-aminobiphenyl 

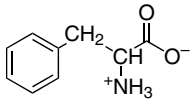
s. Since 4-Methylacetophenone contains more than five carbon atoms, it is insoluble in water. It is also insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution, but soluble in 96% sulfuric acid. Therefore, 4-methylacetophenone is in solubility class N.

4-methylacetophenone 

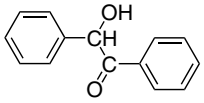
t. Naphthalene is insoluble in water since it contains more than five carbon atoms. It is insoluble in 5% sodium hydroxide solution and 5% hydrochloric acid solution. However, naphthalene is soluble in 96% sulfuric acid, and therefore in solubility class N.

naphthalene 

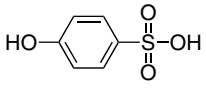
u. Phenylalanine is an amino acid, thus is amphoteric, and soluble in water. Phenylalanine is insoluble in ether and thus in solubility class S_2.

phenylalanine 

v. Benzoin is insoluble in water since it has more than five carbon atoms. It is insoluble in water, 5% sodium hydroxide solution, and 5% hydrochloric acid solution. However, benzoin is soluble in 96% sulfuric acid, and therefore in solubility class N.

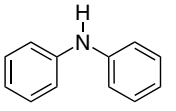
benzoin 

w. As a strong organic acid, 4-hydroxybenzenesulfonic acid is insoluble in water. However, it is soluble in 5% sodium hydroxide solution and 5% sodium bicarbonate solution. 4-Hydroxybenzenesulfonic acid is in solubility class A_1.

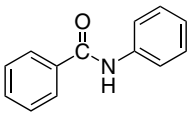
4-hydroxybenzenesulfonic acid 

7. Listed in order from least basic to most basic (see next question).

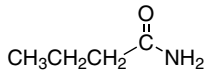
$N, S_1 < B < S_B$



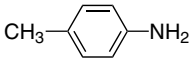
diphenylamine

and 

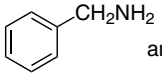
benzanilide

and 

butanamide

< 

4-methylaniline

< 

benzylamine

and $CH_3CH_2CH_2CH_2CH_2NH_2$
pentylamine

8.

Benzanilide	Solubility class	N
Pentylamine	Solubility class	S_B
Diphenylamine	Solubility class	N
Benzylamine	Solubility class	S_B
4-Methylaniline	Solubility class	B
Butanamide	Solubility class	S_1

9. Listed in order from least soluble to most soluble in water.

a. Smaller alcohols are more soluble.

$CH_3CH_2CH_2CH_2OH$ < $(CH_3)_2CHOH$ < CH_3CH_2OH < CH_3OH

1-butanol 2-propanol ethanol methanol

b. More hydroxyl groups increase solubility.

$CH_3CH_2CH_2CH_3$ < $CH_3CH_2CH_2CH_2OH$ < $HOCH_2CH_2CH_2CH_2OH$

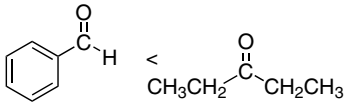
butane 1-butanol 1,2-butanediol

c. Branching increases solubility.

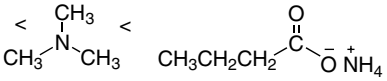
$CH_3CH_2CH_2CH_2OH$ < $CH_3CH(OH)CH_2CH_3$ < $CH_3C(CH_3)_2OH$

1-butanol 2-butanol 2-methyl-2-propanol

d. $N < S_1\text{–}N < S_B < S_2$



benzaldehyde 3-pentanone



triethylamine ammonium butanoate

10. **a.**

Methanol	Solubility class	S_1
Isopropyl alcohol	Solubility class	S_1
Ethanol	Solubility class	S_1
1-Butanol	Solubility class	S_1

b.

Butane	Solubility class	I
1,4-Butanediol	Solubility class	S_2
1-Butanol	Solubility class	S_1

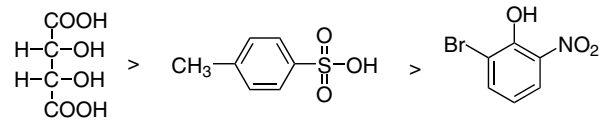
c.

1-Butanol	Solubility class	S_1
2-Methyl-2-propanol	Solubility class	S_1
2-Butanol	Solubility class	S_1

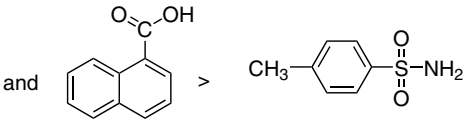
d.

Ammonium butanoate	Solubility class	S_2
3-Pentanone	Solubility class	S_1–N
Benzaldehyde	Solubility class	N
Trimethylamine	Solubility class	S_B

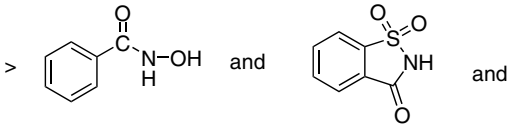
11. The following compounds are listed in order of decreasing activity.



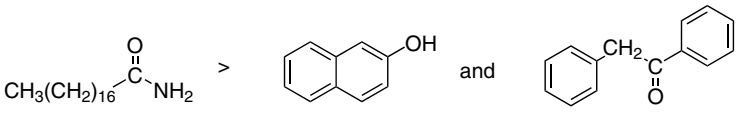
meso-tartaric acid (S_2) > 4-toluenesulfonic acid (S_A) > 2-bromo-6-nitrophenol (A_1)



and 1-naphthoic acid (A_1) > 4-toluene-sulfonamide (A_2)



> benzohydroxamic acid (MN) and saccharin (MN) and



octadecanamide (MN) > 2-naphthol (N) and benzyl phenyl ketone (N)

Chapter 6

Separation of Mixtures

1. a. Pentane – volatile

b. D-glucose – low volatility, with certain exceptions these compounds cannot be distilled at atmospheric pressure

c. Diethylamine – readily distill, many compounds boil below 100 °C

d. 2-Butanone – readily distill, many compounds boil below 100 °C

2. a. Pentane – volatile with steam

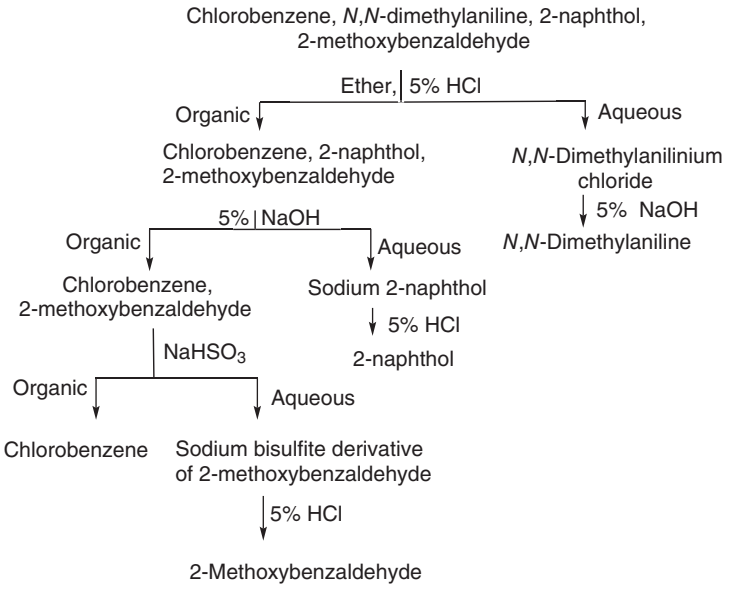
b. D-Glucose – not volatile with steam

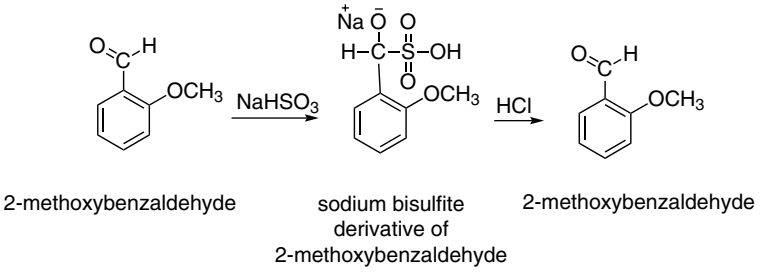
c. Diethylamine – volatile with steam

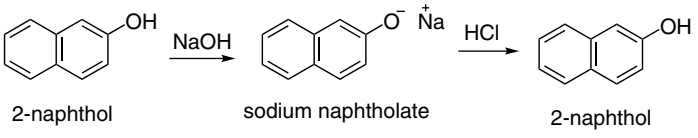
d. 2-Butanone – volatile with steam

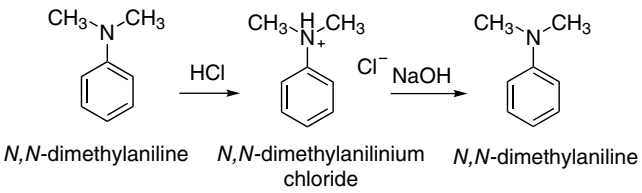
Student Solutions Manual to Accompany The Systematic Identification of Organic Compounds, Ninth Edition.
Christine K. F. Hermann, Terence C. Morrill, Ralph L. Shriner, and Reynold C. Fuson.

3.

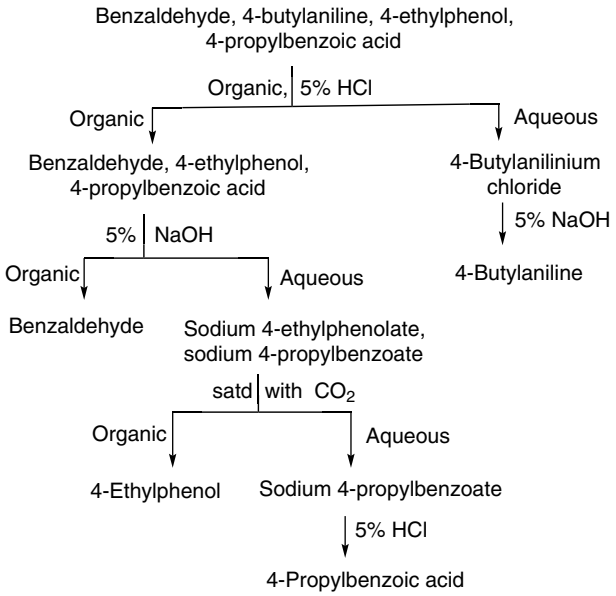

Chlorobenzene, N,N-dimethylaniline, 2-naphthol, 2-methoxybenzaldehyde
Ether, 5% HCl
Organic
Aqueous
Chlorobenzene, 2-naphthol, 2-methoxybenzaldehyde
N,N-Dimethylanilinium chloride
5% NaOH
N,N-Dimethylaniline
5% NaOH
Organic
Aqueous
Chlorobenzene, 2-methoxybenzaldehyde
Sodium 2-naphthol
5% HCl
2-naphthol
NaHSO3
Organic
Aqueous
Chlorobenzene
Sodium bisulfite derivative of 2-methoxybenzaldehyde
5% HCl
2-Methoxybenzaldehyde

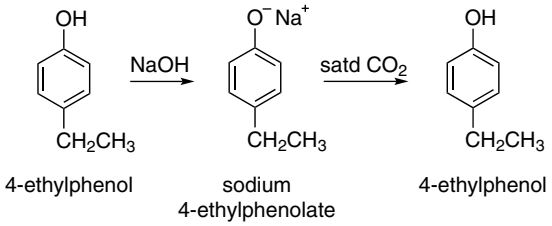

NaHSO3
HCl
2-methoxybenzaldehyde
sodium bisulfite derivative of 2-methoxybenzaldehyde
2-methoxybenzaldehyde

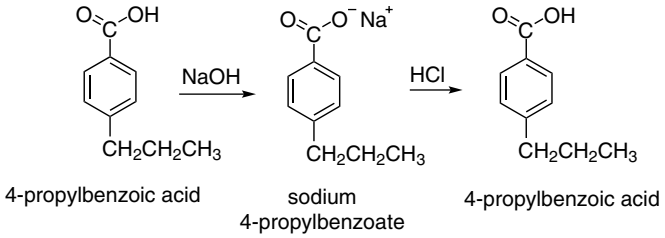

NaOH
HCl
2-naphthol
sodium naphtholate
2-naphthol

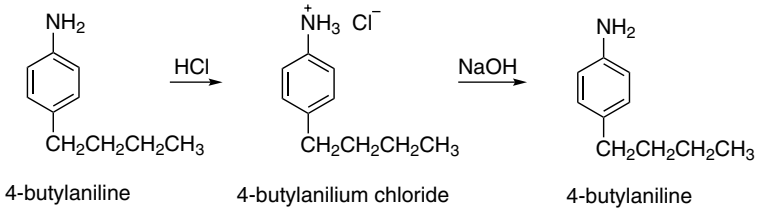

HCl
NaOH
N,N-dimethylaniline
N,N-dimethylanilinium chloride
N,N-dimethylaniline

4.









5. Since glucose is also insoluble in ether, it would be filtered out as Residue 1.